



Aqueous Extract of *Vitex negundo* Leaves as Green Corrosion Inhibitor for the Protection of Carbon Steel in 1N HCl Solution

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Abstract

The corrosion inhibition of carbon steel in 1N HCl containing aqueous extract of *Vitex negundo* leaves (VNL) has been studied using chemical techniques (Weight loss and gasometric methods) and electrochemical techniques (Electrochemical Polarization and electrochemical impedance studies). At the best concentration of 800 ppm of VNL extract provides 79.2% of the inhibition efficiency on carbon steel. The effect of acid concentration on the corrosion reaction showing first order without changing the reaction mechanism, and the results showed that when the concentration of VNL extract increased the rate of carbon steel corrosion is decreased, which indicates that the inhibition of the corrosion process is produced. Electrochemical impedance analysis results showed that the corrosion inhibition of carbon steel occurred mainly by charge transfer. The electrochemical results of polarization showed that the extract of VNL plant act as a mixed type inhibitor and they retarded both anodic and cathodic reactions. The experimental results from chemical and electrochemical studies were fit Langmuir isotherm. Values of the equilibrium constant of adsorption and the standard free energy of adsorption for the extracts are also calculated.

Key words: Carbon steel; Corrosion inhibitors; Hydrochloric acid; Langmuir isotherm; *Vitex negundo*.

1. INTRODUCTION

Carbon steel is mainly employed in engineering materials, metal processing equipment, construction, marine applications, petroleum production, refining and chemical processing. (Badr, 2009). It is also used in sea water desalination plants. However, several problems arise due to corrosion because of factors such as temperature, pH, aggressive environments, seawater-air aerosols, corrosive gases, etc. (Malik *et al.* 1994). Moreover, acid solutions which are used in industries for acid pickling, industrial acid cleaning and acid descaling causes corrosion (Zhng and Hua, 2009). There are many techniques used to minimize the corrosion of iron due to attack by acids. One of the techniques is the use of inhibitors, which are mainly organic compounds containing hetero atoms in their aromatic ring (N, P, S, O) or long chain carbon with multiple bonds showed good potential corrosion inhibition efficiency (Ravichandran and Rajendran, 2005; Atul Kumar, 2008; Hussin and Kassim, 2011). However, they are highly toxic and thus, the need to use naturally occurring and eco-friendly corrosion inhibitors

(Ostovari *et al.* 2009). Plant extracts are important as renewable, environmentally acceptable, readily available corrosion inhibitors because they have a close similarity to those of organic inhibitors (Shivakumar *et al.* 2013; Oguzie, 2010). The extracts derived from natural products such as *Ricinus communis*, *Telfaria occidentalis*, *Zenthoxylum alatum*, *Justicia gendarussa*, *Vitis vinifera*, *Palicourea guianensis*, *Xylopia ferruginea*, *Annona muricata*.L, *Tagetes erecta*, *Stevia rebaudiana*, *Juniper oxycedrus*, *Neolamarckia cadamb*, *Aloes*, *Pavetta indica*, *Haloxylon scoparium pommel* have been studied as effective corrosion inhibitors on carbon steel in acid medium (Sathiyathan *et al.* 2005; Oguzie, 2005; Chauhan and Gunasekaran, 2006; Satapathy *et al.* 2009; Saratha *et al.* 2010; Lebrini, Robert and Roos, 2011; Raja, Pandian Bothi *et al.* 2011; Rosaline Vimala *et al.* 2012; Subha and Saratha, 2012; Cang *et al.* 2012; 2013; Belkhaouda *et al.* 2013; Raja *et al.* 2013; Allaoui *et al.* 2013; Sheeja and Subhashini, 2014).

Vitex negundo Linn. (Verbenaceae) is a woody, aromatic shrub growing to a small tree. It

commonly bears tri- or penta-foliate leaves on quadrangular branches, which give rise to bluish-purple coloured flowers in branched tomentose cymes. It thrives in humid places or along water courses in wastelands and mixed open forests and has been reported to occur in Afghanistan, India, Pakistan, Sri Lanka, Thailand, Malaysia, Eastern Africa and (Vishwannathan and Basavaraju, 2010) Madagascar. It is grown commercially as a crop in parts of Asia, Europe, North America and West Indies.

The present work is devoted to study the inhibition characteristics of *Vitex negundo leaves* (VNL) extract on the corrosion of carbon steel in 1N HCl solution, using weight loss, gasometric, Tafel polarization and AC impedance studies. From this, a suitable mechanism regarding the mode of inhibition was proposed. Surface morphology on the carbon steel with and without inhibitor was made to confirm the adsorptive layer on the surface of carbon steel.

2. EXPERIMENTAL METHOD

2.1 Material preparation

Carbon steel used to this study has the following composition(wt.%): 0.17% C, 0.46% Mn, 0.26% Si, 0.017% S and the remainder iron. Carbon steel coupons with dimension 2 cm x 2 cm x 0.3 cm were used for weight loss and gasometric studies. For tafel polarization studies, a cylindrical rod embedded in teflon with exposed surface area 0.5 cm² was used. The electrode was polished with different grades of emery papers degreased with acetone and rinsed with distilled water. AR grade hydrochloric acid was used for preparing the test solution.

2.2 Preparation of *Vitex negundo leaves* (VNL) extract

Vitex negundo (Nirgundi) leaves were washed in distilled water and dried in an air oven at 60 °C for 3 hr. The dried leaves were ground well and make it well into powder. 10 g of the leaf powder was refluxed in 100 mL of distilled water for 1 hr. Whatmann No.1 filter paper was used to filter the extract and the filtrates were heated on water bath until the moisture content gets evaporated completely (Shivakumar et al. 2013). Corrosion study was performed by using test solution which was prepared by dissolving specified amount of VNL extract in 1N HCl solution.

2.3 Weight loss studies

Weight loss measurements were carried out as described elsewhere (Badr, 2009). From the measured weight loss data, the corrosion rate (mmpy) was calculated using the formula:

$$\text{Corrosion rate (mmpy)} = kW/ATD$$

where, $k = 8.76 \times 10^4$ (constant), W = weight loss in g, A = area in square cm, T = time in hours and $D = 7.85$ in gm / cu.cm.

The percentage inhibition efficiency (IE) and surface coverage (θ) which represent the part of the metal surface covered by the inhibitor molecules were calculated using the following equation:

$$\begin{aligned} \text{Inhibition Efficiency (\%)} &= W_B - W_I / W_B \times 100 \\ \text{Surface coverage (\%)} &= W_B - W_I / W_B \end{aligned}$$

where W_B is the weight loss in the absence of VNL extract, W_I is the weight loss in the presence of VNL extract. From these data, a suitable isotherm was fitted graphically.

2.4 Gasometric studies

The design of the studies as described elsewhere (Sureshkumar et al. 2012). The coupons of carbon steel were suspended from the hook of the glass stopper and were introduced into the sample cell containing 100 mL of 1N HCl solution. At constant atmospheric pressure, 30 °C temperature was maintained constantly throughout the experiments. Volume measurements were made for a period of three hours in all the cases. From the volume of hydrogen gas liberated, the inhibition efficiency was calculated using the formula given below

$$\text{Inhibition efficiency (\%)} = V_0 - V_I / V_I \times 100$$

where V_0 is the volume of hydrogen evolved in the absence and V_I is the volume of hydrogen evolved in the presence of VNL extract in 1N HCl solution.

2.5 Electrochemical polarization studies

Polarization measurements were carried out using electrochemical analyzer (Biologic, VSP, France). Three electrode cells consists of a saturated calomel electrode as reference electrode, platinum foil as auxiliary electrode and carbon steel of 1 cm² area as working electrode was used. Electrochemical polarization measurements were performed from a cathodic potential of -800 mV (Vs SCE) to an anodic potential of -200 mV (Vs SCE) at a scanning rate of 1mV/s. From the Tafel polarization curves, Tafel slopes, corrosion potentials and corrosion current were calculated.

The percentage inhibition efficiency (IE %) was calculated from corrosion current density values using the equation (Subramania et al. 2004):

$$IE (\%) = I_{\text{Corr}} - I_{\text{Corr}}^* / I_{\text{Corr}} \times 100$$

where I_{Corr} and I_{Corr}^* are corrosion current in the absence and presence of VNL extract in 1N HCl solution.

2.6 Electrochemical impedance studies

Impedance measurements were carried out using electrochemical analyzer (Biologic, VSP, France) in the frequency range of 100 kHz to 1 mHz at an applied amplitude of 10 mV. The impedance diagrams are given in Nyquist representation. The inhibition efficiency values were calculated using equation:

$$IE (\%) = R_t^* - R_t / R_t^* \times 100$$

where R_t^* and R_t are the charge transfer resistance in the presence and absence of VNL extract in 1N HCl solution.

2.7 Metallurgical microscopic studies

The carbon steel test coupons were immersed in 1N HCl solution in the absence and presence of VNL extract (800 ppm) for 3 hr. After termination of the experiment, the coupons were washed with distilled water, dried and examined for their surface morphology using metallurgical microscope with the magnification of 1000x.

3. RESULT & DISCUSSION

3.1 Weight loss studies

Fig.1 represents the effect of VNL extract concentration on inhibition efficiency in 1N HCl solution. The VNL extract showed the maximum inhibition efficiency of 79.2% at the best concentration of 800 ppm. Further, the increase in VNL extract concentration did not cause any significant change in the performance of the extract. The values of percentage inhibition efficiency ($IE\%$) and corrosion rate obtained from weight loss method at different concentrations of VNL extract at 308 K are summarized in table 1.

3.2 Effect of immersion time

To assess the stability of inhibitive behavior of VNL extract on a time scale, weight loss measurements were performed in 1N HCl solution in absence and presence of the best concentration of VNL extract for 3 to 24 hrs with 3 hrs interval period of immersion time at temperature 303K. Inhibition efficiency was plotted against immersion time is shown in fig. 2. This figure shows that the inhibition efficiency of the extract was decreased with increasing

immersion time from 3 to 24 hrs. Higher inhibition efficiency of 79.2% (table 2) at 3 hrs reflects the strong adsorption of constituents present in the VNL extract on the carbon steel surface, resulting in a more protective layer formed at carbon steel and hydrochloric acid solution interface. But at 24 hrs, the inhibition efficiency decreased to 76.4% which shows desorption process started slowly at increasing immersion time.

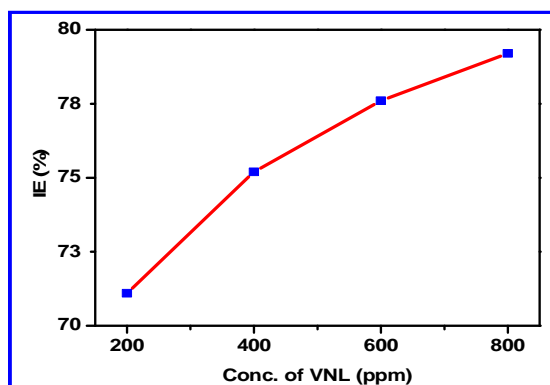


Fig. 1: Variation of inhibition efficiency with various concentrations of VNL extract on carbon steel in 1N HCl solution

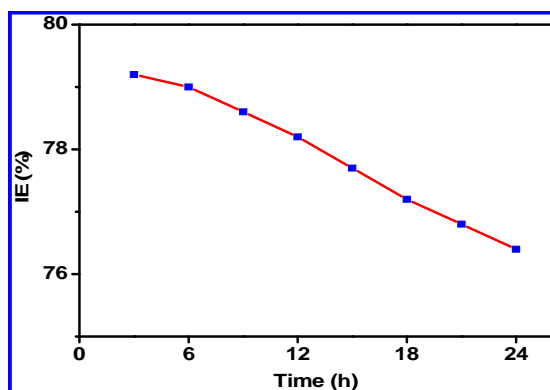


Fig. 2: Effect of immersion time on percentage inhibition efficiency of carbon steel in 1N HCl at 30°C in presence of the best concentration (800 ppm) of VNL extract

3.3 Gasometric measurements

Table 3 shows inhibition efficiency of VNL extract from 200 ppm to 800 ppm using hydrogen evolution method. The maximum inhibition efficiency of 79.7% is obtained at the concentration of 800 ppm of VNL extract, since the hydrogen evolution volume is decreased from 7.4 to 1.5 mL.

3.4 Tafel Polarization studies

Polarization curves for carbon steel in the absence and presence of the best concentration of VNL

extract in 1N HCl solution are shown in fig. 3. Highest inhibition efficiency of 80.0% obtained at the best concentration of VNL extract. The extrapolation of Tafel straight line allows the calculation of the corrosion current density (I_{corr}). The values of I_{corr} , the corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_a and b_c) and inhibition efficiency (IE %) are given in table 4.

The change in b_a and b_c values are shown in table 4. It indicates that the adsorption of VNL extract modifies the mechanism of anodic dissolution as well as cathodic hydrogen evolution. From fig. 3, it is clear that both the cathodic and anodic reactions are inhibited and the inhibition efficiency increases with the best concentration of VNL extract (800 ppm) in acid solution. From table 4, it is clear that there was no definite trend in the shift of E_{corr} values in the presence of 800 ppm.

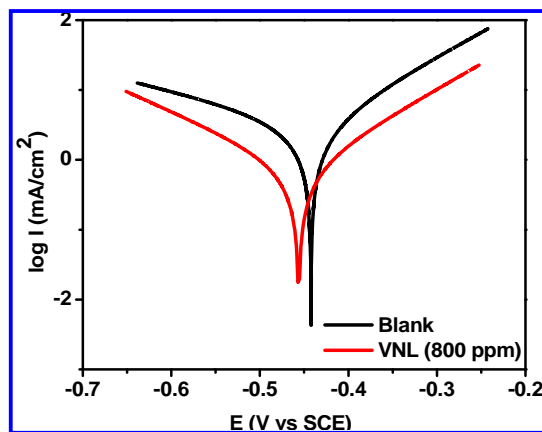


Fig. 3: Polarization curves for carbon steel in 1N HCl solution in the absence and presence of the best concentration of VNL extract

Table 1. Corrosion parameters obtained from weight loss measurements for carbon steel in 1N HCl containing various concentrations of VNL extract

Conc. of VNL extract (ppm)	Initial weight (g)	Final weight (g)	Weight Loss (gm)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
Blank	3.7096	3.6601	0.0495	20.4581	----	----
200	4.0759	4.0902	0.0143	5.8959	71.1	0.711
400	3.7957	3.8080	0.0123	5.0713	75.2	0.752
600	3.7774	3.7885	0.0111	4.5765	77.6	0.776
800	3.8937	3.9040	0.0103	4.2467	79.2	0.792

Table 2. Effect of immersion time on percentage inhibition efficiency of carbon steel in 1N HCl at 30 °C in presence of the best concentration (800 ppm) of VNL extract

Conc. of VNL extract (ppm)	Inhibition Efficiency (%) : Time (h)							
	3	6	9	12	15	18	21	24
800	9.2	79.0	78.6	78.2	77.7	77.2	76.8	76.4

Table 3. Inhibition efficiency obtained from gasometric measurements for carbon steel in 1N HCl containing various concentrations of VNL extract at 30 °C

Concentration of VNL Extract (% in v/v)	Volume of Hydrogen Gas evolved (mL)	Inhibition Efficiency (%)
Blank	7.4	--
200	2.1	71.6
400	1.8	75.7
600	1.6	78.3
800	1.5	79.7

3.5 AC impedance studies

Impedance spectra for carbon steel in 1N HCl solution in absence and presence of the best concentration of VNL extract are shown fig. 4. It can be observed from the Nyquist plot that a single semicircle has been observed is attributed to charge transfer takes place at electrode/solution interface. The impedance parameters such as double layer capacitance (C_{dl}), charge transfer resistance (R_t) and IE% are listed in table 5. It is clear from the table that at optimum concentration (800 ppm) of VNL extract, the C_{dl} value tends to decrease and the inhibition efficiency increases. The decrease in C_{dl} is due to increase in the thickness of the electrical double layer suggested that VNL extract function by adsorption at the metal/solution interface. It is apparent from Nyquist plots that the impedance response of carbon steel in inhibited HCl solution has significantly changed after the addition of VNL extract in acid solution and that the impedance of inhibited substrate increases at optimum concentration (800 ppm) of VNL extract. Increase in R_t value indicates the adsorbed extract forms a protective film on the carbon steel surface which becomes a barrier to hinder the mass and charge transfer processes (Lebrini *et al.* 2008). The Nyquist plots showed that at the best concentration (800 ppm) of VNL extract, charge transfer resistance increases and double layer capacitance decreases. From the table 5, it is clear that the 800 ppm of VNL extract which gives R_t value of $90.8 \Omega \text{ cm}^2$ in 1N HCl solution with 78.44% of inhibition efficiency. The data obtained from AC-impedance are in good agreement with those obtained from weight loss method.

3.6 Effect of Temperature

The effect of temperature on corrosion rate was studied in 1N HCl, both in the absence as well as in the presence of the best concentration of VNL extract at different temperatures 30 °C to 90 °C for exploring the activation energy of the corrosion process and the thermodynamic function of adsorption of VNL extract. As it can be seen in the table 6, raising the temperature leads to a higher corrosion rate. It is seen that the investigated VNL extract has inhibiting properties at all the studied temperatures. But the values of inhibition efficiency for VNL extract decreased from 79.2% to 70.6% with temperature increase at the VNL concentration of 800 ppm (fig. 5).

Table 5. Impedance parameters for the corrosion of carbon steel in 1N HCl in the absence and presence of the best concentration of VNL extract at 30 °C

Conc. VNL Extract (ppm)	R_t ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F/cm}^2$)	Inhibition Efficiency (%)
Blank	20.65	116.9	-
800 ppm	90.8	25.74	78.44

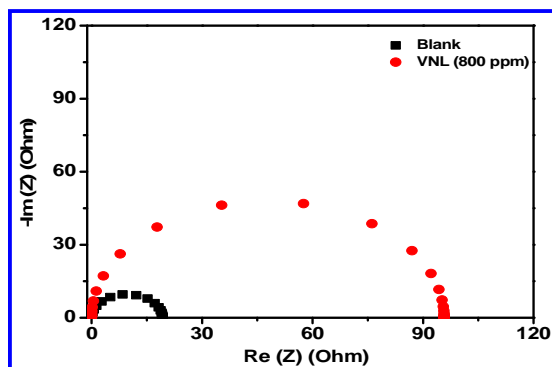


Fig. 4: Impedance diagrams for carbon steel in 1N HCl solution in the absence and presence of the best concentration of VNL extract

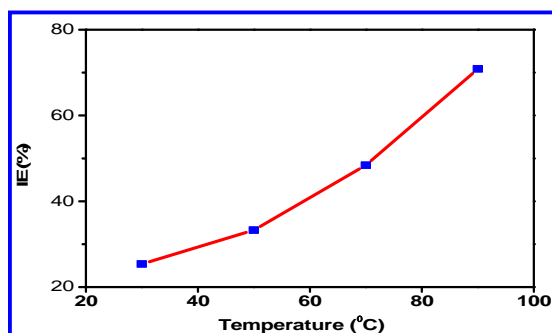


Fig. 5: Effect of temperature on the corrosion inhibition efficiency of carbon steel in 1N HCl in presence of the best concentration (800ppm) of VNL extract

Table 6. Corrosion of carbon steel in the absence and presence of the best concentration of VNL extract in 1N HCl at different temperatures obtained by weight loss method

Conc. of VNL extract (ppm)	Temperature (°C)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
Blank	30	122.46	---
	50	152.92	---
	70	189.46	---
	90	241.60	---
800	30	25.39	79.2
	50	33.27	78.2
	70	48.40	74.4
	90	70.87	70.6

3.7 Thermodynamic studies and corrosion mechanism

The activation parameters for the corrosion process were calculated from Arrhenius-type plot according to the following equation (Fouda *et al.* 2014):

$$\ln r = A - E_a / RT$$

where E_a is the apparent activation corrosion energy, R is the universal gas constant, A is the pre-

exponential factor and T is the absolute temperature. Arrhenius plots for the corrosion of carbon steel in the case of VNL extract is shown in fig. 6.

The calculated values of activation energy (E_a), enthalpy of adsorption (ΔH°), free energy of adsorption (ΔG°) and entropy of adsorption (ΔS°) for carbon steel in the absence and presence of the best concentration of VNL extract in 1N HCl solution are shown in table 7. Inspection of the data shows that the activation energy is lower in the absence of inhibitor than in its presence. It has been reported that higher E_a in presence of VNL extract on carbon steel in comparison with blank solution is typically showing physisorption (Lakshmi Prabha *et al.* 2012). From table 7, the positive signs of the enthalpy (ΔH°) reflect the endothermic nature of the carbon steel dissolution process. Adsorption of the VNL extract on carbon steel was a slow process and its disordered manner was confirmed by low and positive values of (ΔS°) (Rosaline Vimala *et al.* 2011).

The standard free energy of adsorption was calculated using the following equation:

$$\Delta G^\circ_{\text{ads}} = -RT \ln (K/55.5)$$

where the value of 55.5 is the concentration of water in solution expressed in mole L^{-1} and K is the surface coverage area.

The negative values of ΔG° suggest that the adsorption of the VNL extract on the carbon steel surface is spontaneous. Generally, the values of ΔG° around or less than -20 kJ mol^{-1} are associated with the electrostatic interaction between charged molecules and the charged metal surface (physisorption); while those around or higher than -40 kJ mol^{-1} mean charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of metal bond (chemisorption).

Table 7. Calculated values of activation energy (E_a), enthalpy of adsorption (ΔH°), free energy of adsorption (ΔG°) and entropy of adsorption (ΔS°) for carbon steel in the absence and presence of the best concentration of VNL extract in 1N HCl solution

Conc. of VNL extract (ppm)	Temp (K)	E_a (kJ/mol)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
Blank	303	---	---	---	---
	323	9.04	---	6.35	---
	343	9.87	---	7.02	---
	363	12.58	---	9.56	---
800	303	---	-8.30	---	---
	323	10.99	-8.85	8.30	0.053
	343	17.26	-9.39	14.41	0.069
	363	19.73	-9.95	16.71	0.073

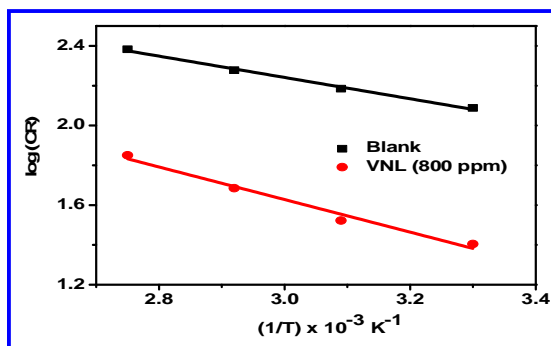


Fig. 6: Arrhenius plots for carbon steel immersed in 1N HCl solution in the absence and presence of the best concentration (800ppm) of VNL extract

The ΔG° values are around -10 kJ mol^{-1} which means that the adsorption of the VNL extract on the carbon steel surface belongs to the physisorption and the adsorptive film has an electrostatic character (Shyamala and Arulanantham, 2008).

3.8 Phytochemical constituents of VNL extract

The major constituents present in the VNL extract are some flavonoids (Sathiamoorthy *et al.* 2007). The structure of some flavonoids present in VNL extract is shown in fig. 7. These compounds get adsorbed on the carbon steel surface and form a barrier for charge and mass transfers leading to a decrease in the interaction of carbon steel with the corrosive acid environment. As a result, the corrosion rate of carbon steel was decreased

3.9 Adsorption isotherm

The inhibition efficiency of VNL extract mainly depends on their adsorption ability on the metal surface. Generally, adsorption isotherm provides information regarding the interaction between the inhibitor and the metal surface (Saleh and Atia, 2006). The degree of surface coverage (θ) obtained from weight loss method was determined as a function of inhibitor concentration were used to obtain adsorption isotherms (Fouda *et al.* 2014). Different adsorption isotherms were tested for their fit to the experimental data. According to these results, it can be concluded that the best description of the adsorption behaviour of VNL extract can be explained by Langmuir adsorption isotherm. It is given by the following equation (Li, 2009):

$$C/\theta = 1/K + C$$

A plot of C/θ versus C gives a straight line with unit slope suggesting that the adsorption of VNL extract on the surface of carbon steel in 1N HCl solution follows Langmuir adsorption isotherm (fig. 8). Langmuir's isotherm assumes that the

adsorption of organic molecule on the metal surface is monolayer and the adsorbed molecules occupy only one site and there is no interaction with other adsorbed species.

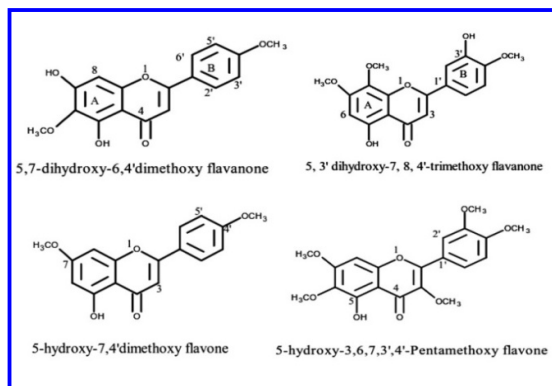


Fig. 7: Structure of some flavonoids present in VNL extract

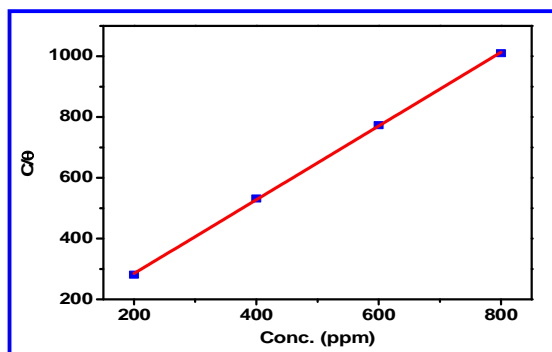


Fig. 8: Langmuir adsorption isotherm plot for the adsorption of various concentrations of VNL extract on the surface of carbon steel in 1N HCl solution

3.10 Metallurgical microscope studies

Metallurgical micrographs obtained for the carbon steel immersion in 1N HCl solution in the absence and presence of the best concentration of VNL extract for a period of 3 hr (fig. 9a & 9b).

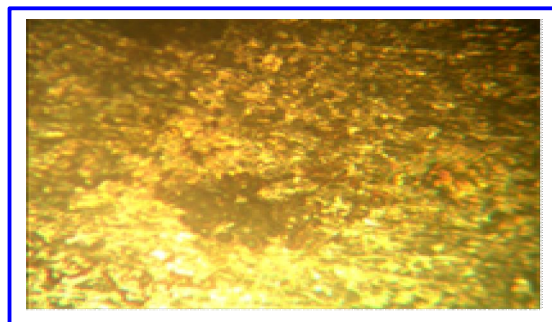


Fig. 9 (a): Metallurgical microscope image of carbon steel immersed in 1N HCl solution (blank)

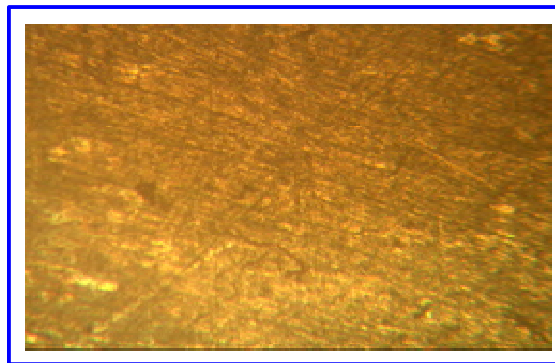


Fig. 9(b): Metallurgical microscope image of carbon steel immersed in 1N HCl solution containing 800 ppm of VNL extract

A comparison has been done with the morphology, uninhibited carbon steel showed more pits and rough surface, while inhibited carbon steel showed smooth and less corroded surface. This may be due to adsorption of phytochemical constituents present in VNL extract on carbon steel.

4. CONCLUSION

The corrosion behaviour of carbon steel has a marked dependence on concentration, temperature and immersion time. A correlation between the corrosion rate and the state of the carbon steel surface in HCl solution is observed for various immersion periods. VNL extract acts as good corrosion inhibitor for carbon steel in acid medium. It behaves as mixed type inhibitor since its E_{corr} values are not shifted significantly with respect to blank. Good agreement is observed between the values obtained by weight loss, gasometric, and electrochemical polarization and impedance studies. Percentage inhibition efficiency of VNL extract was temperature dependent and its addition led to decrease in the activation energy of corrosion. Thermodynamic parameters revealed that the corrosion inhibition by VNL extract is due to the formation of physisorption and spontaneous process. The adsorption of VNL extract onto carbon steel surface follows the langmuir adsorption isotherm. Metallurgical microscopic analysis further confirmed that corrosion is inhibited in the presence of VNL extract.

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